

Tacticities of Copoly(vinyl ester)s Obtained by Radical Polymerization

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ABSTRACT: Tacticity simulations of poly(vinyl acetate-*co*-vinyl propionate) [poly(VAc-*co*-VPr)], poly(vinyl acetate-*co*-vinyl decanoate) [poly(VAc-*co*-VD)] and poly(vinyl acetate-*co*-vinyl pivalate) [poly(VAc-*co*-VP)] were tried by a terminal model. Cotacticities for vinyl acetate (VAc)/vinyl pivalate (VPr) and vinyl acetate (VAc)/vinyl decanoate (VD) were well simulated and coisotactic parameters for these systems could be estimated. But the tacticities of poly(VAc-*co*-VP) could not be well simulated by the terminal model indicating penultimate effect and simulation by penultimate model was tried.

KEY WORDS Tacticity Simulation / Terminal Model / Copoly(vinyl ester)
/ Radical Polymerization / Coisotactic Parameter / Penultimate Effect /

It is well known that cotacticities of copolymers vary with monomers and their compositions, and those for poly(styrene-*co*-methyl methacrylate) are well investigated.¹⁾ However, as it has been difficult to determine the tacticities of polymers and copolymers of vinyl esters, the studies on tacticities and cotacticities have not progressed with a few exceptions on those of poly(vinyl ester)s like poly(vinyl acetate) (poly(VAc)) which is easily converted to poly(vinyl alcohol) (PVA) by saponification. Although it is easy to determine the tacticities of PVA, it was very difficult to saponify poly(vinyl ester) with large ester groups like poly(vinyl pivalate) [poly(VP)], and studies on those have not progressed.²⁾

Recently we found a good method to saponify poly(VP), and found the method to be useful for poly- and copoly(vinyl ester)s with large ester group³⁾. It makes possible to determine the tacticities of poly(vinyl propionate) [poly(VPr)], poly(vinyl decanoate)

[poly(VD)], poly(VP) and their copolymers by assuming them to be equal to those of corresponding PVAs which are easily determined. We reported the tacticities of PVAs⁴⁾, and in this paper we simulated the tacticities of poly(vinyl acetate-*co*-vinyl propionate) [poly(VAc-*co*-VPr)], poly(vinyl acetate-*co*-vinyl decanoate) [poly(VAc-*co*-VD)], and poly(vinyl acetate-*co*-vinyl pivalate) [poly(VAc-*co*-VP)] and estimated the coisotactic parameters.

EXPERIMENTAL

Copolymerization and Tacticities

Monomers and initiator were purified as written in the previous paper.⁴⁾ Photo-copolymerizations in bulk were carried out at 0°C by using α, α' -azobisisobutyronitrile (AIBN) for VAc/VPr and VAc/VP, and initiator-free photo-emulsion copolymerizations were carried out at 0°C for VAc/VD as written in the

Table I. Results of copolymerizations^a of VAc(M₁) with vinyl esters at 0°C

M ₂	VAc mol%	conversion	VAc mol% ^b	Triad tacticity ^c		
	in feed	%	in copolymer	<i>I</i>	<i>H</i>	<i>S</i>
VPr	0		0	18.5	50.0	31.6
	22.8	6.0	20.6	18.8	50.0	31.2
	44.0	5.7	42.7	19.9	50.0	30.1
	54.1	5.8	51.3	19.6	50.1	30.3
	63.9	5.9	59.7	20.1	50.1	29.7
	82.5	6.6	80.9	21.8	50.2	28.0
	100		100	22.4	49.9	27.7
VD	0	34.0	0	18.0	49.8	32.2
	21.4	36.0		20.4	49.1	30.5
	51.2	30.3	52.0	20.2	49.7	30.1
	71.0	74.0	67.8	21.7	49.3	29.0
	78.6	36.3	78.7	22.7	48.5	28.8
	85.1	59.3	86.0	20.9	49.3	29.8
	90.7	51.5		21.7	50.2	28.1
	95.7	79.8	95.4	21.3	49.6	29.1
	100		100	22.3	50.0	27.7
	VP	0		0	12.8	48.9
28.5		9.8	21.0	12.9	52.1	35.0
51.6		7.2	43.7	14.2	51.6	34.2
61.5		6.6	62.5	16.3	50.9	32.8
70.6		4.1	70.9	18.1	51.5	30.4
86.5		6.6	87.9	18.5	51.4	30.1
100			100	22.4	49.9	27.7

^a Photo-copolymerizations of VAc with VPr and VP by using AIBN were carried out in bulk at 0°C, and initiator-free photo-emulsion copolymerizations of VAc with VD were carried out at 0°C.

^b Copolymer composition were determined by ¹H-NMR spectrum of copolymer.

^c Triad tacticities of copolymers were estimated from the ¹H-NMR spectrum of PVA derived from the copolymers.

previous papers.^{3,4} Copolymer composition was determined from ¹H-NMR spectrum of the copolymer. Monomer reactivity ratios were obtained by the Fineman-Ross plots. Triad tacticities of copolymers were determined from ¹H-NMR spectra of PVA derived by saponification³ from the respective copolymers. The data are listed in Table I. Computer simulation of tacticities was carried out on the basis of these data by the terminal model which is established as follows (eq 1—9).

Terminal Model

Triad tacticities of homo-polymer are expressed as eq 1, 2, and 3 for isotactic-(*I*), heterotactic-(*H*), and syndiotactic-triad (*S*),

respectively.

$$I = \sigma^2 \quad (1)$$

$$H = 2\sigma(1 - \sigma) \quad (2)$$

$$S = (1 - \sigma)^2 \quad (3)$$

where σ is isotactic parameter. Applying eq 1, 2, and 3 for copolymerization, cotacticities are expressed by eq 4, 5, and 6.

$$I = \sum \sum \sum \sigma_{ij} \sigma_{jk} m_i P_{ij} P_{jk} \quad (4)$$

$$H = \sum \sum \sum (1 - \sigma_{ij})(1 - \sigma_{jk}) m_i P_{ij} P_{jk} \quad (5)$$

$$S = \sum \sum \sum \{ (1 - \sigma_{ij}) \sigma_{jk} + \sigma_{ij} (1 - \sigma_{jk}) \} m_i P_{ij} P_{jk} \quad (6)$$

Equations 4, 5, and 6 are converted to eq 7, 8,

Table II. Values of r_1 , r_2 , and (co)isotactic parameters

M_2	r_1	r_2	σ_{11}	σ_{12}	or	σ_{21}	σ_{22}
VPr	0.90	1.13	0.474	0.438		0.448	0.438
VD	1.10	0.90	0.474	0.451		0.451	0.433
VP	0.88	1.17	0.474	0.434		0.383	0.381

and 9 according to Mayo-Lewis equation.

$$I = F(\sigma_{11}r_1F + \sigma_{21})(\sigma_{11}r_1F + \sigma_{12}) / (r_1F + 1)(r_1F^2 + 2F + r_2) + (\sigma_{22}r_2 + \sigma_{12}F) / (F + r_2)(r_1F^2 + 2F + r_2) \quad (7)$$

$$H = 1 - (I + S) \quad (8)$$

$$S = 1 + I - 2\{\sigma_{11}r_1F^2 + (\sigma_{12} + \sigma_{21})F + \sigma_{22}r_2\} / (r_1F^2 + 2F + r_2) \quad (9)$$

where r_i , monomer reactivity ratio, m_i , monomer mole fraction in copolymer, P_{ij} , probability for M_iM_j sequence, σ_{ij} , probability for M_iM_j sequence being meso diad (when $i=j$, isotactic parameter, and when $i \neq j$, coisotactic parameter), F , monomer mole fraction in feed.

The values of r_1 and r_2 were obtained by Fineman-Ross plots of the data in Table I and σ_{11} , σ_{22} are assumed to be equal to those of respective homopolymerization obtained from the data in Table I, and are shown in Table II. The values of I , H , and S could be calculated for various F values by varying σ_{12} and σ_{21} values. The values of σ_{12} and σ_{21} which make the sum of the square of the differences between experimental and calculated I , H , and S values minimum are considered to be coisotactic parameters.

RESULTS AND DISCUSSION

Trial by Terminal Model

The results simulated on the basis of the values in Tables I and II are shown in Figures 1, 2, 3, and in Table II. In Figures 1 and 2, the solid lines indicate simulated values and circles indicate experimental results. As shown in the

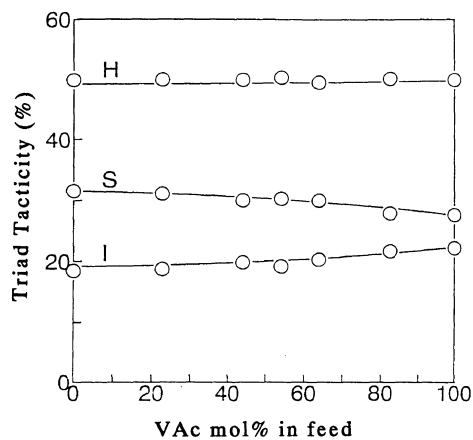


Figure 1. Relations between triad tacticities and feed monomer composition for poly(VAc-co-VPr) obtained radically at 0°C. O, experimental results; solid line, simulation curve by the terminal model.

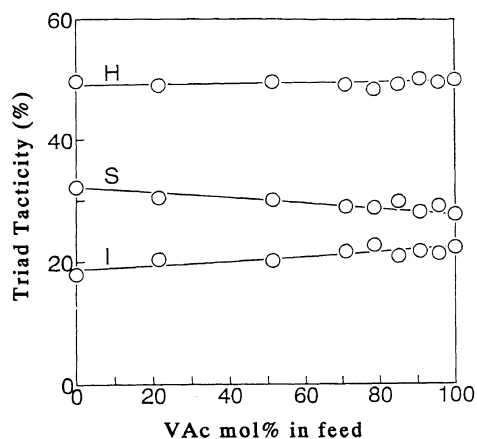


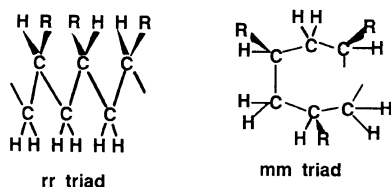
Figure 2. Relations between triad tacticities and feed monomer composition for poly(VAc-co-VD) obtained radically at 0°C. O, experimental results; solid line, simulation curve by the terminal model.

figures, the simulation curves for VAc/VPr and VAc/VD are in good agreement, and σ_{12} and σ_{21} values for them are almost equal indicating

the terminal model to be valid. Although we can not distinguish σ_{12} and σ_{21} in the equation, the agreement is considered to support the terminal model. As conversions in the copolymerizations of VAc and VD are high, the values of r_1 and r_2 determined by Fineman-Ross method may be inaccurate. In order to investigate the influence of errors in r_1 and r_2 , some calculations were carried out by varying r_1 and r_2 , and marked variation in curves and coisotactic parameters was not observed.

On the other hand, the values of σ_{12} and σ_{21} for VAc/VP which make the sum of the square of the difference between experimental and calculated I , H , and S are not in good agreement. The simulation curves by the values do not fit with experimental plots (Figure 3, broken line). So the terminal model is not good for copolymerization of VAc with VP, and new model is essential.

We consider that the structures of transition state for the mm and rr propagation are similar to those of mm and rr triad which are shown as following.



As shown above, rr triad shows a stretched structure, the distance between the first ester substituent and the third one is large, and the interaction between these two substituents is not so much. The mm triad shows a helical structure to cancel out a steric strain, the distance between the first ester substituent and the third one is almost the same as that between the second and the first or the third one, and the interaction between these two substituents, especially in the case of bulky substituent as VP, is important.

We considered that the interaction between the first and the third substituent in mm triad is a cause for the marked deviation in the

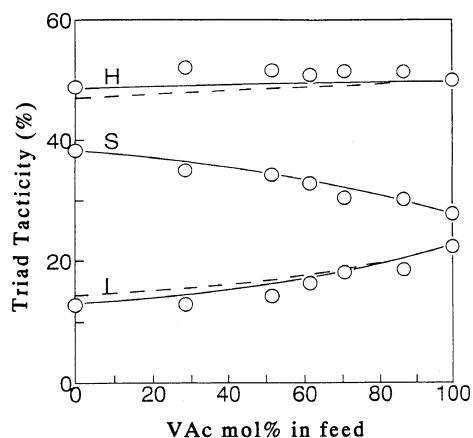


Figure 3. Relations between triad tacticities and feed monomer composition for poly(VAc-co-VP) obtained radically at 0°C. \circ , experimental results; broken line, simulation curve by the terminal model; solid line, simulation curve by the penultimate model.

Table III. Values of σ and σ' for VAc, VPr, VD, and VP

	VAc	VPr	VD	VP
σ	0.474	0.438	0.433	0.381
σ'	0.471	0.423	0.416	0.336

terminal model simulation from experimental for VAc/VP system, and the interaction between the first and the third substituent should be accounted into the simulation as penultimate effect, and tried simulation as follows.

Trial by Penultimate Model

In this study, penultimate effects were assumed as follows; 1) When a monomer adds to the propagating unit forming racemo structure with the penultimate unit and makes rm structure, isotactic and coisotactic parameters do not vary. 2) When a monomer adds to the propagating unit forming meso structure with the penultimate unit and makes mm structure, the isotactic and coisotactic parameters change from σ to σ' .

Taking into account the penultimate effects, eq 10, 11, and 12 are derived from eq 1, 2, and 3.

Table IV. Values of (co)isotactic parameters for poly(VAc-co-VP) estimated by penultimate model, M_1 ; VAc

σ_{11}	σ'_{11}	σ_{12}	σ'_{12}	σ_{21}	σ'_{21}	σ_{22}	σ'_{22}
0.474	0.471	0.426	0.408	0.383	0.345	0.381	0.336

$$I = \sigma\sigma' \quad (10)$$

$$H = \sigma(1 - \sigma') + (1 - \sigma)\sigma \quad (11)$$

$$S = (1 - \sigma)^2 \quad (12)$$

The values of isotactic parameters for VAc, VPr, VD, and VP are calculated on the basis of experimental data by eq 10, 11, and 12, and are shown in the following table.

The relation between σ and σ' in Table III is shown as eq. 13, which is considered to show penultimate effect in homopolymerization (although we have not had physical explanation). Then eq 10, 11, and 12 are converted to eq 14, 15, and 16, respectively.

$$\sigma' = 1.448\sigma - 0.209 \quad (13)$$

$$I = \sigma(1.448\sigma - 0.209) \quad (14)$$

$$H = \sigma(1.209 - 1.448\sigma) + (1 - \sigma)\sigma \quad (15)$$

$$S = (1 - \sigma)^2 \quad (16)$$

Applying eq 14 to cotacticities, eq 17 is derived.

$$I = \sum \sum \sum \sigma_{ij} \sigma'_{jk} m_i P_{ij} P_{jk} \quad (17)$$

Applying Mayo-Lewis equation to eq 17, eq. 18 is derived.

$$I = F(\sigma_{11}r_1F + \sigma_{21})(\sigma'_{11}r_1F + \sigma'_{12})/(r_1F + 1)(r_1F^2 + 2F + r_2) + (\sigma_{22}r_2 + \sigma_{21}F)(\sigma_{22}r_2 + \sigma_{12}F)/(F + r_2)(r_1F^2 + 2F + r_2) \quad (18)$$

To make equations simple, $\sigma'_{ij} = 1.448\sigma_{ij} - 0.209$ was assumed to hold in the copolymerization, and eq 18 is converted to eq 19. In this method, as S does not change from terminal model, eq 9 is used for simulation. However, the isotactic parameter (σ_{11} , σ_{22})

should be determined by eq 16. Then $H = 1 - (I + S)$.

$$I = F(\sigma_{11}r_1F + \sigma_{21})\{1.448(\sigma_{11}r_1F + \sigma_{12}) - 0.209(r_1F + 1)\}/(r_1F + 1)(r_1F^2 + 2F + r_2) + (\sigma_{22}r_2 + \sigma_{12}F)\{1.448(\sigma_{22}r_2 + \sigma_{21}F) - 0.209(r_2 + F)\}/(F + r_2)(r_1F^2 + 2F + r_2) \quad (19)$$

According to these equation simulations were carried out and simulation curves (solid line in Figure 3) and coisotactic parameters (Table IV) were obtained. Although the curves are improved, they do not fit with experimental data completely and the assumption for penultimate model would be not valid and should be reconsidered. We are developing a method and will show the details in the near future.

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